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## **Supplementary Information for**

## Infiltrating Molecular Gatekeepers with Coexisting Molecular-Solubility

## and 3D-Intrinsic-Porosity into Microporous Polymer Scaffold for Gas

Separation

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#### Section S1. Supplementary methods

### 1. Fabrication of control membrane samples

*AOPIM-1 membranes infiltrated with*  $H_2SO_4$ : As each SCA4 molecule can donate twice as many protons as  $H_2SO_4$  molecule does, the ideal mole ratio of  $H_2SO_4$  to AOPIM1 polymer content was doubled so as to resemble similar infiltration conditions as AOPIM1-SCA4 membranes. As AOPIM1-SCA4-2% and AOPIM1-SCA4-3% were chosen for the comparison, 0.8 mg and 1.3 mg of concentrated  $H_2SO_4$  aqueous solution were added to MeOH for treating 65 mg of as-cast AOPIM1 samples over 24 hours so that the ideal mole ratio of  $H_2SO_4$  to AOPIM1 polymer content was about 7.8% (2 × 3.9%) and 12.4% (2 × 6.2%), respectively. The drying procedure was identical as before, and the as-prepared membranes were named as AOPIM1-H<sub>2</sub>SO<sub>4</sub>-2% and AOPIM1-H<sub>2</sub>SO<sub>4</sub>-3%.

*AOPIM1 membranes physically blended with SCA4 or CA4t*: Each of SCA4 and CA4t powders were dissolved in the DMF solvent together with AOPIM1 polymers at a mole ratio of 2.44% and 4.96%, respectively, for thorough physical blending to fabricate the mixed matrix membranes (MMMs). They were named as AOPIM1-M-SCA4-2% and AOPIM1-M-CA4t-5%, respectively, where 'M' stands for 'mixing'. The rest of solution-casting procedures were identical to the AOPIM1 membranes as described in Section 1.3.1.

### 2. Aging protocol

The testing of gas separation performance of all samples was completed within maximally 3 days after their fabrication so as to ensure 'freshness' and minimal influence from physical aging on the performance. AOPIM1 and AOPIM1-SCA4 membrane samples were kept under vacuum at room temperature when not in use, and were mounted to the permeation cell for testing their aged performance at the 30<sup>th</sup> day and the 60<sup>th</sup> day from fabrication. The performance tests for each of these aged samples were also completed within 3 days.

#### 3. Insoluble content measured by redissolution

The insoluble content in AOPIM1, AOPIM1-SCA4 and AOPIM1-H<sub>2</sub>SO<sub>4</sub> membranes were determined by measuring the re-dissolved mass of these membranes in DMF. 50 mg of each membrane sample was re-dissolved into 10 g DMF and the solution-mixture was stirred overnight. Then the solution-mixtures were filtered by 5  $\mu$ m PTFE syringe filters to remove insoluble contents, and the filtrates were cast into dense membranes via identical procedures as described above in Section 1.3.1. The dried mass of the re-cast membranes was measured and the percentage weight difference from the initial 50 mg was taken as the insoluble content in the respective samples.

### 4. Characterizations

Liquid-state 400 MHz <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopy (Bruker Avance III HD 400 MHz NMR Spectrometer) was employed to confirm the chemical structure of the AOPIM1 polymer and probe into the specific proton signal changes caused by the hydrogenbond or proton-transfer interactions. The samples were dissolved in DMSO-d<sub>6</sub> for testing. The functional groups of the membrane samples and their changes after SCA4 infiltration were analysed by the Bruker Vertex 70FM Fourier transform infrared spectroscopy (FTIR) which was operated in the attenuated total reflectance (ATR) mode with a wavenumber ranging from 500 to 4000 cm<sup>-1</sup>. Bonding signals of the key functionalities and interactions were investigated by the X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra<sup>DLD</sup>, Kratos Analytical Ltd., UK) operated with a monochromatic X-ray source of 15 kV and 100 W. The binding energy spectra for element N 1s were obtained, and the relevant data analysis and processing were carried out in the PeakFit software. Thermogravimetric analyses (TGA) were conducted by a Shimazu Thermal Analyzer (DTG-60AH/TA-60WS/FC-60A) to characterize the thermal stability of membrane samples under a nitrogen-purged environment (60 ml / min flow rate). The heating protocol used for all samples was 10°C / min ramp from room temperature to 100 °C, 20 min hold at 100 °C, followed by 7 °C / min ramp to 800 °C.

The changes in packing efficiency and interchain spacing of the AOPIM1 polymers after SCA4 infiltration were examined by a Bruker D8 Advance X-ray diffractometer (XRD) with the X-ray radiation source being Cu K- $\alpha$  (1.54 Å wavelength) and the diffraction angles ranging between 5° and 30°. The average d-spacing was evaluated based on the Bragg's Law (  $n\lambda = 2dsin\theta$ ) where *n* is an integer (1, 2, 3),  $\lambda$  represents the wavelength of the X-ray radiation source, d denotes the average interchain/intersegmental distance between adjacent polymer chains and  $\theta$  is the measured X-ray diffraction angle. The distribution of sulfur (S) elements which directly represent the SCA4 molecules within the membrane samples was examined by the scanning electron microscope coupled with energy-dispersive X-ray spectroscopy (SEM-EDX). AOPIM1-SCA4-3% was analysed as a representative sample with both surface and cross-section being scanned for S elements. The mechanical strength, including tensile strain, maximum tensile stress and Young's modulus, of all the AOPIM1-SCA4 samples were tested by an Instron® 5542 tensile testing machine equipped with a 2701 series of pneumatic grip control system and the Bluehill® Universal operation platform. The average sample dimensions used for the mechanical tests were  $25 \pm 5 \,\mu\text{m}$  in thickness,  $1.5 \pm 0.5 \,\text{mm}$  in width and  $15 \pm 3 \,\mu\text{m}$ mm in length. The density of AOPIM1-SCA4 membrane samples was measured by a liquid displacement method based on the Archimedes principle using n-hexane and that of SCA4 powders was determined by an AccuPyc II 1340 helium pycnometer system.

# Section S2. Complete occluded solvent removal and AOPIM1-SCA4 membrane's thermal stability by thermogravimetric analysis (TGA)

The effectiveness of occluded casting solvent removal by solvent exchange with MeOH was corroborated by the thermogravimetric analysis (TGA) under inert N<sub>2</sub> environment. From the TGA plots shown in Fig. S2a, the as-cast AOPIM1 samples experienced a much greater weight loss from about 150 °C onwards due to the evaporation of trapped DMF solvents, whereas the solvent-exchanged ones were thermally stable until around 200 °C (amidoxime functionalities began to degrade afterwards) and obtained a very similar fractional weight loss pattern to that

of a control sample whose trapped solvents were completely removed by vacuum heating (fabrication details of this control sample were shown Section 1.3.1).

Also, the thermal stability of AOPIM1 membranes after SCA4 infiltration was found practically invariant up to at least 200 °C (Fig. S3b) which was robust for most industrial gas separations. Thermal degradation occurred afterwards due to the decomposition labile amidoxime functionalities instead of SCA4 which only started to decompose at a higher temperature of around 300 °C.

# Section S3. Characteristic sulfonic group signals and hydrogen bonding in Fouriertransform infrared (FTIR) spectroscopy

The Fourier-transform infrared (FTIR) spectra, shown in Fig. S3, illustrated a gradual increase in the transmittance intensity of the characteristic O=S=O symmetric stretching signal (1027 cm<sup>-1</sup>) as the degree of SCA4 infiltration within the AOPIM1 membranes became higher. This was an evidence of the successful SCA4 incorporation via our proposed post-fabrication infiltration (PFI) method. The gradual attenuation of stretching signals of -NH<sub>2</sub> (V<sub>s</sub>= 3337 cm<sup>-1</sup>, V<sub>as</sub> = 3474 cm<sup>-1</sup>) after SCA4 infiltration also reflected its active involvement in proton-transfer interactions.

### Section S4. Sulfur element distribution observed by SEM-EDX

The distribution of sulfur elements across the surface of the sample appeared to be slightly more concentrated than the cross-section due to its proximity and larger exposed area to the bulk SCA4-MeOH solution, which was reasonable. Indeed, the sulfur line scan (Fig. S10) evidenced the higher concentration of SCA4 across a about 2  $\mu$ m-thick regions from both top and bottom surfaces of an AOPIM1-SCA4-3% sample. However, for the central region which was about 22  $\mu$ m thick, although the concentration of SCA4 was lower than that near the surface due to higher mass transfer resistance, it is still significant with a very uniform distribution through the whole central region with good SCA4 infiltration all the way to the very center of this overall 26  $\mu$ m-thick dense film sample.

# Section S5. AOPIM1 chemical structure confirmation and control sample bonding comparison by <sup>1</sup>H NMR

The chemical structure of AOPIM1 polymer was characterized by <sup>1</sup>H NMR spectroscopy as shown in Fig. S4, and it agreed nicely with the literature.<sup>[1]</sup> In the control sample, AOPIM1-M-CA4t-5% membrane, CA4t could only use its -OH groups at the bottom rim to interact with the amidoxime moieties unlike SCA4 who can wield its pendent sulfonic groups. Such interaction was naturally weak due to greater steric hindrance and high tendency of these bottom -OH groups being involved in hydrogen bonding among themselves. Therefore, from this comparison, it was most possible that the observed strong influence on the proton signals of -C=N-OH was majorly contributed by the sulfonic groups of SCA4.

### Section S6. Changes in the density and insoluble content of AOPIM1-SCA4 membranes

As summarize by Table S2, the bulk density of the AOPIM1-SCA4 membranes slightly increased with the degree of infiltration due to the mildly tightened chain packing and the accommodation of additional molecules within micropores. Strong ionic or hydrogen-bond bridging effect by SCA4 also affected the insoluble content in the AOPIM1-SCA4 membranes. As also shown in Table S2, the percentage weight of insoluble content increased with the degree of infiltration, which indicated greater extensiveness of hydrogen-bond and ionic interactions between the polymer chains and SCA4 molecules.

### Section S7. Correlation between diffusivity and FFV

A linear plot of log (Diffusivity) against 1/FFV was shown in Fig. S9 to demonstrate the strong correlation between the diffusion-type gas transport and the available free volume in membranes. Permeability of  $H_2$  was used in place of its diffusivity as the solubility of  $H_2$  should remain largely invariant with the degree of infiltration.

### Section S8. Effect of bound water on gas separation performance

It has been shown that polymer containing sulfonic groups tend to sorb and bind water in the atmosphere, and high temperature vacuum pretreatment is one method to dry the membranes.<sup>[2]</sup> In order to better remove any possible bound water from the AOPIM1-SCA4 membranes, several previously fabricated but well-kept AOPIM1-SCA4-5% samples (have an age of 330 days at the time of retesting) were pretreated at 100 °C under high vacuum for 24 hours followed by the original 20-hour 35 °C stabilizing under vacuum before permeation tests. Comparison samples without pretreatment were also tested. As summarized in Table S9, the pretreated AOPIM1-SCA4-5% samples, which should have their bound water or other lightly adsorbed species all removed by the 24 hours of 100 °C vacuum heating, showed very similar pure-gas permeabilities for all the fives gases tested including H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>, as compared with the untreated samples. This similarity in gas separation performance between the two differently treated batches of samples suggested that the influence of bound water in AOPIM1-SCA4 membranes should be, even at the highest degree of SCA4 infiltration (i.e. 5%), quite minimal on the gas transport properties of these membranes for these five gases.

### References

[1] H. A. Patel, C. T. Yavuz, Noninvasive functionalization of polymers of intrinsic microporosity for enhanced CO<sub>2</sub> capture, *Chem. Comm.* **48**, 9989-9991 (2012).

[2] M. Mukaddam, E. Litwiller, I. Pinnau, Gas sorption, diffusion, and permeation in Nafion, *Macromolecules* 49, 280-286 (2016).



Fig. S1. Calibration curve between residual SCA4 mass and the titrant volume.



**Fig. S2. Thermogravimetric analysis (TGA) plots of various AOPIM1 and AOPIM1-SCA4 samples.** They confirmed (a) complete removal of occluded DMF and (b) the thermal stability of AOPIM1-SCA4 membranes.



**Fig. S3.** Fourier-transform infrared (FTIR) spectra of AOPIM1, AOPIM1-SCA4 membranes and SCA4 powders.



**Fig. S4.** <sup>1</sup>H NMR spectra for the confirmation of AOPIM1 synthesis and the observation of hydrogen bonding between SCA4 and the oxime group.



Fig. S5. Sorption isotherms of SCA4 solid powders for  $N_2$ ,  $CH_4$  and  $CO_2$  pure gases obtained at 35 °C and a pressure up to 10 bar. Data points were fitted to a dual-mode. sorption model.



Fig. S6. Gas separation performance after physical aging. Changes in pure-gas  $H_2$  permeability and  $H_2/N_2$  and  $H_2/CH_4$  selectivity were plotted against aging time to demonstrate the performance stability against aging.



Fig. S7. Upper bound plots for equimolar  $H_2/CH_4$  mixed-gas performance. 0% - 5% indicates the degree of SCA4 infiltration, solid data points are for pure gas, hollow data points are for mixed gas, dotted arrow lines are drawn to guide eye.



Fig. S8.  $H_2/CO_2$ ,  $O_2/N_2$ , and  $CO_2/CH_4$  pure-gas separation performance at 35 °C and 3.5 bar. The upper bound plots were shown here for pure-gas (a)  $H_2/CO_2$  (comparison with high-performance literature data obtained mostly at 35 °C), (b)  $O_2/N_2$  and (c)  $CO_2/CH_4$  separations (respective degree of SCA4 infiltration labeled next to the data points, dotted arrow lines are drawn to guide eyes); (d) legends for literature high-performance  $CO_2/CH_4$  data points (number in parentheses means the number of aging days, number at the end of each name means pyrolysis temperature in °C).



Fig. S9. Correlation between diffusivity and fractional free volume for various gases.  $H_2$  permeability is used in place of diffusivity and 0% - 5% means the degree of SCA4 infiltration.



**Fig. S10. Distribution of SCA4 molecules across the membrane.** The superimposed SEM image and sulfur line scan across the surface of AOPIM1-SCA4-3% membrane (left) and the sulfur element concentration over depth plot (right).

	Before Infusion <sup>a</sup>		After	After Infusion						
Sample	pH Value	Volume of Titrant <sup>b</sup> (ml)	pH Value	Volume of Titrant (ml)	Initial SCA4 (mg)	Ideal Mole Ratio	Residual SCA4 (mg)	SCA4 infused into membranes (mg)	Total Sample Dried Weight (mg)	Actual Mole Ratio
AOPIM	6.87	0	6.87	0	0	0%	0	0	57.3	0%
AOPIM1- SCA4-1%	1.55	1.4	6.81	0.4	1.2	1.5%	0.4	0.8	58.6	0.99%
AOPIM1- SCA4-2%	1.21	3.2	1.70	1.2	3.1	3.8%	1.2	1.9	58.4	2.44%
AOPIM1- SCA4-3%	1.03	5.0	1.29	2.3	5.0	6.2%	2.3	2.7	59.6	3.48%
AOPIM1- SCA4-5%	0.81	10.1	1.01	6.5	10.3	12.7%	6.6	3.7	60.9	4.96%

Table S1. Determination of degree of infiltration by titration.

<sup>*a*</sup> For generating the calibration curve (Figure S1)

<sup>b</sup> Titrant = 20mg NaOH in 100ml Methanol solution

Samples	Bulk Density (g/cm <sup>3</sup> )	Breaking Elongation (%)	Ultimate Tensile Stress (MPa)	Young's Modulus (MPa)	Insoluble Content (%)
AOPIM1	$1.187\pm0.011$	$11.2\pm0.9$	$32.2\pm3.0$	887 ± 111	52.1%
AOPIM1- SCA4-1%	$1.205\pm0.012$	13.1 ± 2.0	$34.1\pm4.1$	$939\pm88$	59.7%
AOPIM1- SCA4-2%	$1.215\pm0.009$	$14.6 \pm 1.8$	$34.6\pm5.1$	$986\pm128$	72.2%
AOPIM1- SCA4-3%	$1.233\pm0.022$	$13.9\pm1.7$	$33.8\pm2.7$	$1019\pm112$	76.9%
AOPIM1- SCA4-5%	$1.234\pm0.019$	$12.1 \pm 1.9$	$32.4\pm1.6$	$877\pm147$	78.0%
AOPIM1- H <sub>2</sub> SO <sub>4</sub> -2%	-	-	-	-	85.6%
AOPIM1- H <sub>2</sub> SO <sub>4</sub> -3%	-	-	-	-	92.5%

 Table S2. Membrane bulk density, mechanical strength and insoluble content.

**Table S3.** PALS lifetimes and corresponding free volume radii obtained at ambient temperature and pressure.

Sample	τ <sub>3</sub> (ns)	I <sub>3</sub> (%)	R3 (Å)	τ <sub>4</sub> (ns)	I4 (%)	R4 (Å)	FFV(%)	Var.
AOPIM1	$1.28\pm0.07$	$8.15\pm0.46$	$2.07\pm0.10$	$2.87\pm0.04$	$12.58\pm0.45$	$3.55\pm0.02$	$4.79\pm0.22$	1.03
AOPIM1-SCA4- 1%	$1.27\pm0.10$	$8.07\pm0.37$	$2.06\pm0.13$	$2.84\pm0.05$	$12.43\pm0.65$	$3.53\pm0.02$	$4.65\pm0.30$	0.96
AOPIM1-SCA4- 2%	$1.23\pm0.13$	$7.92\pm0.44$	$2.01\pm0.17$	$2.76\pm0.05$	$12.17\pm0.70$	$3.47\pm0.03$	$4.31\pm0.31$	1.01
AOPIM1-SCA4- 3%	$1.22\pm0.12$	$7.83\pm0.60$	$1.99\pm0.17$	$2.74\pm0.04$	$12.06\pm0.54$	$3.45\pm0.02$	$4.20\pm0.24$	1.00
AOPIM1-SCA4- 5%	$1.19\pm0.14$	$7.66\pm0.58$	$1.94\pm0.19$	$2.70\pm0.06$	$11.93\pm0.77$	$3.43\pm0.03$	$4.04\pm0.33$	0.99

**Table S4.** Summary of permeability and selectivity for  $H_2$ ,  $O_2$ ,  $N_2$ ,  $CH_4$  and  $CO_2$  at 35 °C and 3.5 bar.

		Perme	ability (B	arrer)			Selectivity						
	$H_2$	<b>O</b> <sub>2</sub>	$N_2$	$\mathrm{CH}_4$	$CO_2$	$H_2/N_2$	$\mathrm{H_2/CH_4}$	$H_2/CO_2$	$O_2/N_2$	$CO_2/N_2$	$\rm CO_2/CH_4$		
PIM-1	1738 ± 155	$\begin{array}{c} 510 \ \pm \\ 81 \end{array}$	149 ± 15	$\frac{198}{37} \pm$	$\begin{array}{c} 3127 \ \pm \\ 403 \end{array}$	11.7 ± 0.5	$\begin{array}{c} 8.8 \pm \\ 0.3 \end{array}$	$\begin{array}{c} 0.560 \ \pm \\ 0.02 \end{array}$	$\begin{array}{c} 3.42\ \pm\\ 0.20\end{array}$	$\begin{array}{c} 21.0\ \pm\\0.7\end{array}$	$\begin{array}{c} 15.8 \ \pm \\ 0.4 \end{array}$		
AOPIM1	$\begin{array}{c} 926 \ \pm \\ 16 \end{array}$	$\begin{array}{c} 194 \ \pm \\ 16 \end{array}$	47.3 ± 2.5	$\begin{array}{c} 42.3 \ \pm \\ 2.9 \end{array}$	$\begin{array}{c} 1073 \ \pm \\ 30 \end{array}$	19.6 ± 0.7	$\begin{array}{c} 22.0 \ \pm \\ 1.2 \end{array}$	$\begin{array}{c} 0.864 \ \pm \\ 0.03 \end{array}$	$\begin{array}{c} 4.09 \ \pm \\ 0.16 \end{array}$	$\begin{array}{c} 22.7 \pm \\ 0.1 \end{array}$	$\begin{array}{c} 25.4 \ \pm \\ 0.6 \end{array}$		
AOPIM1- SCA4-1%	866 ± 16	140 ± 5	27.4 ± 3.4	22.9 ± 2.0	718 ± 32	32.2 ± 4.9	$\begin{array}{c} 38.1 \pm \\ 4.0 \end{array}$	$\begin{array}{c} 1.21 \ \pm \\ 0.07 \end{array}$	$5.18 \pm 0.60$	26.5 ± 2.4	31.5 ± 1.4		
AOPIM1- SCA4-2%	$\begin{array}{c} 781 \ \pm \\ 15 \end{array}$	$\begin{array}{c} 62.1 \pm \\ 2.8 \end{array}$	$\begin{array}{c} 8.57 \ \pm \\ 0.11 \end{array}$	$\begin{array}{c} 3.35 \ \pm \\ 0.09 \end{array}$	$\begin{array}{c} 257 \pm \\ 10 & 1 \end{array}$	91.0 ± 1.7	$\begin{array}{c} 233 \ \pm \\ 2 \end{array}$	$\begin{array}{c} 3.04 \ \pm \\ 0.06 \end{array}$	$\begin{array}{c} 7.24 \ \pm \\ 0.32 \end{array}$	$\begin{array}{c} 30.0 \ \pm \\ 1.2 \end{array}$	$\begin{array}{c} 76.7 \pm \\ 0.9 \end{array}$		
AOPIM1- SCA4-3%	$\begin{array}{c} 693 \\ 57 \end{array}$	$\begin{array}{c} 53.0 \pm \\ 6.9 \end{array}$	$\begin{array}{c} 7.16 \ \pm \\ 0.79 \end{array}$	$\begin{array}{c} 2.67 \pm \\ 0.31 \end{array}$	$\begin{array}{c} 223 \pm \\ 17 \end{array}$	97.2 ± 5.1	$\begin{array}{c} 260 \ \pm \\ 14 \end{array}$	$\begin{array}{c} 3.11 \ \pm \\ 0.04 \end{array}$	$\begin{array}{c} 7.39 \ \pm \\ 0.45 \end{array}$	$\begin{array}{c} 31.3 \pm \\ 1.5 \end{array}$	$\begin{array}{c} 83.9 \pm \\ 5.4 \end{array}$		
AOPIM1- SCA4-5%	542 ± 51	$\begin{array}{c} 34.4 \pm \\ 5.4 \end{array}$	$\begin{array}{c} 4.53 \ \pm \\ 0.42 \end{array}$	$\begin{array}{c} 1.83 \ \pm \\ 0.37 \end{array}$	151 ± 25	$\frac{120}{1}\pm$	$\frac{302}{32}\pm$	$\begin{array}{c} 3.65 \pm \\ 0.36 \end{array}$	$\begin{array}{c} 7.55 \ \pm \\ 0.47 \end{array}$	$\begin{array}{c} 33.1 \pm \\ 2.9 \end{array}$	$\begin{array}{c} 83.0 \pm \\ 4.9 \end{array}$		

		N <sub>2</sub>			CH4			CO <sub>2</sub>			
	k <sub>D</sub> (cm <sup>3</sup> (STP)/cm <sup>3</sup> bar)	<i>C</i> ′ <sub>H</sub> (cm <sup>3</sup> (STP)/cm <sup>3</sup> )	b (bar-1)	k <sub>D</sub> (cm <sup>3</sup> (STP)/cm <sup>3</sup> bar)	<i>C</i> ' <sub>H</sub> (cm <sup>3</sup> (STP)/cm <sup>3</sup> )	b (bar-1)	k <sub>D</sub> (cm <sup>3</sup> (STP)/cm <sup>3</sup> bar)	C' <sub>H</sub> (cm <sup>3</sup> (STP)/cm <sup>3</sup> )	b (bar-1)		
AOPIM1	0.63	29.5	0.14	1.46	41.4	0.33	2.54	43.3	1.00		
AOPIM1- SCA4-1%	1.36	11.7	0.86	2.08	27.7	0.68	2.58	44.2	1.04		
AOPIM1- SCA4-2%	1.25	12.7	0.56	1.97	29.9	0.66	2.54	46.6	1.03		
AOPIM1- SCA4-3%	1.66	10.3	0.72	2.17	31.2	0.64	2.78	45.1	1.06		
AOPIM1- SCA4-5%	1.50	12.3	0.64	2.09	29.0	0.66	2.47	46.2	1.05		
SCA4	0.48	9.6	1.25	1.04	19.4	1.50	1.04	12.3	1.67		

**Table S5.** Dual-mode sorption fitting constants for  $N_2$ ,  $CH_4$  and  $CO_2$  at 35 °C and a pressure up to 10 bar.

**Table S6.** Summary of gas transport parameters, including solubility (measured from sorption isotherms) and diffusivity for  $N_2$ ,  $CH_4$  and  $CO_2$  at 35 °C and 3.5 bar.

Sample	<b>Pure Gas Permeability</b> ( <i>Barrer</i> )				Solut [cm <sup>3</sup> (STP)	oility Coeffic )/cm³ membr	c <b>ient</b> rane bar]	<b>Diffusivity Coefficient</b> $(\times 10^7 \text{ cm}^2/\text{s})$			
	$N_2$	$\mathrm{CH}_4$	$CO_2$		$N_2$	$\mathrm{CH}_4$	$CO_2$	$N_2$	$\mathrm{CH}_4$	$CO_2$	
AOPIM1	47.3	42.3	1073	-	3.50	7.89	12.2	1.02	0.402	6.60	
AOPIM1-SCA4-1%	27.4	22.9	718		3.87	7.63	12.5	0.531	0.225	4.31	
AOPIM1-SCA4-2%	8.57	3.35	257		3.63	7.91	13.0	0.177	0.032	1.49	
AOPIM1-SCA4-3%	7.16	2.67	223		3.91	8.32	13.0	0.138	0.024	1.28	
AOPIM1-SCA4-5%	4.53	1.83	151		3.91	7.83	12.9	0.087	0.018	0.881	

**Table S7.** Mixed-gas separation performance for equimolar  $H_2/CH_4$  mixture at 35 °C and 7 bar feed pressure.

	Permeabili	ty (Barrer)	Selectivity
	$H_2$	$\mathrm{CH}_4$	$H_2/CH_4$
AOPIM1	$609\pm24$	$130\pm19$	$4.78\pm0.73$
AOPIM1-SCA4-1%	$567\pm26$	$67.2\pm6.7$	$8.49\pm0.71$
AOPIM1-SCA4-2%	$543\pm8$	$13.7\pm1.2$	$40.2\pm4.0$
AOPIM1-SCA4-3%	$470\pm34$	$6.08\pm0.72$	$79.4\pm7.7$
AOPIM1-SCA4-5%	$393\pm32$	$3.46\pm0.65$	$115 \pm 11$

		Perr	neability	(Barr)		Selectivity						
Test Samples	$H_2$	$O_2$	$N_2$	$\mathrm{CH}_4$	$CO_2$	$H_2/N_2$	$H_2/CH_4$	$H_2/CO_2$	$O_2/N_2$	$CO_2/N_2$	$\rm CO_2/\rm CH_4$	
PIM-1	1738 ± 155	$\begin{array}{c} 510 \pm \\ 81 \end{array}$	149 ± 15	$\begin{array}{c} 198 \pm \\ 37 \end{array}$	$\begin{array}{r} 3127 \pm \\ 403 \end{array}$	11.7 ± 0.5	$\begin{array}{c} 8.8 \pm \\ 0.3 \end{array}$	$\begin{array}{c} 0.560 \pm \\ 0.02 \end{array}$	$\begin{array}{c} 3.42 \ \pm \\ 0.20 \end{array}$	$\begin{array}{c} 21.0 \ \pm \\ 0.7 \end{array}$	$\begin{array}{c} 15.8 \pm \\ 0.4 \end{array}$	
AOPIM1	$\begin{array}{c} 926 \ \pm \\ 16 \end{array}$	$\begin{array}{c} 194 \ \pm \\ 16 \end{array}$	$\begin{array}{c} 47.3 \ \pm \\ 2.5 \end{array}$	$\begin{array}{c} 42.3 \pm \\ 2.9 \end{array}$	$\begin{array}{c} 1073 \ \pm \\ 30 \end{array}$	$\begin{array}{c} 19.6 \ \pm \\ 0.7 \end{array}$	$\begin{array}{c} 22.0 \ \pm \\ 1.2 \end{array}$	$\begin{array}{c} 0.864 \pm \\ 0.03 \end{array}$	$\begin{array}{c} 4.09\ \pm\\ 0.16\end{array}$	$\begin{array}{c} 22.7 \ \pm \\ 0.1 \end{array}$	$\begin{array}{c} 25.4 \pm \\ 0.6 \end{array}$	
(1) Functional Control	ity											
AOPIM1-SCA4- 5%	$\begin{array}{c} 542 \pm \\ 51 \end{array}$	34.4 ± 5.4	$\begin{array}{c} 4.53 \ \pm \\ 0.42 \end{array}$	$\begin{array}{c} 1.83 \ \pm \\ 0.37 \end{array}$	151 ± 25	$\begin{array}{c} 120 \ \pm \\ 1 \end{array}$	$\begin{array}{c} 302 \pm \\ 32 \end{array}$	$\begin{array}{c} 3.65 \ \pm \\ 0.36 \end{array}$	$\begin{array}{c} 7.55 \ \pm \\ 0.47 \end{array}$	$\begin{array}{c} 33.1 \pm \\ 2.9 \end{array}$	$\begin{array}{c} 83.0 \pm \\ 4.9 \end{array}$	
AOPIM1-M- CA4t-5%	$\begin{array}{c} 900 \ \pm \\ 32 \end{array}$	175 ± 5	44.1 ± 5.4	$\begin{array}{c} 40.8 \pm \\ 0.5 \end{array}$	$\begin{array}{c} 1044 \ \pm \\ 21 \end{array}$	$\begin{array}{c} 20.6 \ \pm \\ 1.8 \end{array}$	$\begin{array}{c} 22.0 \ \pm \\ 0.5 \end{array}$	$\begin{array}{c} 0.862 \pm \\ 0.013 \end{array}$	$\begin{array}{c} 4.01 \ \pm \\ 0.37 \end{array}$	$\begin{array}{c} 23.9 \pm \\ 2.4 \end{array}$	$\begin{array}{c} 25.6 \pm \\ 0.2 \end{array}$	
(2) Method Co	ontrol											
AOPIM1-SCA4- 2%	$\begin{array}{c} 781 \pm \\ 15 \end{array}$	$\begin{array}{c} 62.1 \ \pm \\ 2.8 \end{array}$	$\begin{array}{c} 8.57 \pm \\ 0.11 \end{array}$	$\begin{array}{c} 3.35 \ \pm \\ 0.09 \end{array}$	$\begin{array}{c} 257 \ \pm \\ 10 \end{array}$	$\begin{array}{c} 91.0 \ \pm \\ 1.7 \end{array}$	$\begin{array}{c} 233 \ \pm \\ 2 \end{array}$	$\begin{array}{c} 3.04 \ \pm \\ 0.06 \end{array}$	$\begin{array}{c} 7.24 \ \pm \\ 0.32 \end{array}$	$\begin{array}{c} 30.0 \ \pm \\ 1.2 \end{array}$	$\begin{array}{c} 76.7 \pm \\ 0.9 \end{array}$	
AOPIM1-M- SCA4-2%	$\begin{array}{c} 644 \ \pm \\ 11 \end{array}$	94.0 ± 4.9	21.1 ± 1.5	17.7 ± 1.1	538 ± 15	30.6 ± 2.3	36.3 ± 2.6	$\begin{array}{c} 1.20 \ \pm \\ 0.05 \end{array}$	$\begin{array}{c} 4.47 \ \pm \\ 0.07 \end{array}$	$\begin{array}{c} 25.6 \pm \\ 1.0 \end{array}$	$\begin{array}{c} 30.4 \ \pm \\ 1.0 \end{array}$	
(3) Cavity Co	ntrol											
AOPIM1-H <sub>2</sub> SO <sub>4</sub> - 2%	$\begin{array}{c} 887 \pm \\ 51 \end{array}$	$\frac{162}{12}\pm$	39.5 ± 3.5	36.7 ± 4.7	938 ± 127	$\begin{array}{c} 22.5 \ \pm \\ 0.8 \end{array}$	$\begin{array}{c} 24.4 \ \pm \\ 1.9 \end{array}$	$\begin{array}{c} 0.96 \ \pm \\ 0.08 \end{array}$	$\begin{array}{c} 4.10\ \pm\\ 0.06\end{array}$	$\begin{array}{c} 23.6 \pm \\ 1.2 \end{array}$	$\begin{array}{c} 25.6 \pm \\ 0.2 \end{array}$	
AOPIM1-H <sub>2</sub> SO <sub>4</sub> - 3%	762 ± 21	$\begin{array}{c} 123 \ \pm \\ 10 \end{array}$	29.9 ± 2.3	23.3 ± 3.6	679 ± 47	25.5 ± 1.1	32.8 ± 3.2	$\begin{array}{c} 1.12\ \pm\\ 0.04\end{array}$	$\begin{array}{c} 4.13 \ \pm \\ 0.02 \end{array}$	22.7 ± 0.2	29.2 ± 1.9	

**Table S8.** Summary of pure-gas separation performance for all control samples obtained at 35  $^{\circ}$ C and 3.5 bar.

**Table S9.** Pure-gas separation performance of AOPIM1-SCA4-5% membranes after 100 °C vacuum pretreatment at 35 °C and 3.5 bar feed pressure.

		Perm	reability (B	Barr)				Sele	ctivity		
	$H_2$	$O_2$	$N_2$	$\mathrm{CH}_4$	$CO_2$	$H_2/N_2$	$\mathrm{H_2/CH_4}$	$\mathrm{H_2/CO_2}$	$O_2/N_2$	$CO_2/N_2$	$\rm CO_2/\rm CH_4$
AOPIM1	926± 16	194± 16	47.3± 2.5	42.3± 2.9	$\begin{array}{c} 1073 \pm \\ 30 \end{array}$	19.6± 0.7	$\begin{array}{c} 22.0\pm\\ 1.2 \end{array}$	$\begin{array}{c} 0.864 \pm \\ 0.03 \end{array}$	$\begin{array}{c} 4.09\pm\\ 0.16\end{array}$	22.7± 0.1	$\begin{array}{c} 25.4 \pm \\ 0.6 \end{array}$
AOPIM1- SCA4-5% (fresh)	$542\pm \\51$	$\begin{array}{c} 34.4 \pm \\ 5.4 \end{array}$	$\begin{array}{c} 4.53 \pm \\ 0.42 \end{array}$	1.83± 0.37	151± 25	$\frac{120\pm}{1}$	$\begin{array}{c} 302\pm\\ 32\end{array}$	$\begin{array}{c} 3.65 \pm \\ 0.36 \end{array}$	$\begin{array}{c} 7.55 \pm \\ 0.47 \end{array}$	33.1± 2.9	83.0± 4.9
With pre-treatme followe	ent: 100°C i ed by 35°C i	ınder vacuun ınder vacuun	n for 24 h, n in cell for	20 h							
AOPIM1- SCA4-5% (330 days)	474± 18	$\begin{array}{c} 25.5 \pm \\ 1.0 \end{array}$	2.41± 0.14	1.17± 0.09	93.7± 4.9	197± 9	$\begin{array}{c} 407 \pm \\ 15 \end{array}$	5.06± 0.20	10.6±0.4	38.8± 2.3	$\begin{array}{c} 80.3 \pm \\ 2.0 \end{array}$
Without pre-treatment: only 35 °C under vacuum in cell for 20 h											
AOPIM1- SCA4-5% (330 days)	$\begin{array}{c} 462 \pm \\ 15 \end{array}$	$\begin{array}{c} 25.6\pm\\ 0.6 \end{array}$	$\begin{array}{c} 2.52 \pm \\ 0.10 \end{array}$	$\begin{array}{c} 1.09 \pm \\ 0.16 \end{array}$	$\begin{array}{c} 86.8\pm\\ 3.8 \end{array}$	$\frac{183\pm}{16}$	424± 25	$\begin{array}{c} 5.33 \pm \\ 0.16 \end{array}$	$\begin{array}{c} 10.13 \pm \\ 0.2 \end{array}$	$\begin{array}{c} 34.4 \pm \\ 1.4 \end{array}$	79.7± 3.3